

DIRECT MEASUREMENTS OF THE VOLCANIC MATTER IN THE LOWER ATMOSPHERE

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Some results of measurements of the structure characteristics and chemical composition of aerosol of volcanic origin carried out with the balloonborne, two-stage impactors are discussed. These results allowed us to reveal some peculiarities in the microstructure and element composition of the aerosol. Such elements as As, Sb, Hg, Au, Cu are indicative of the presence of volcanic substance in atmospheric aerosol and thus can be used for studying the spreading of volcanic aerosols.

1. INTRODUCTION

Volcanic eruptions as a source of the aerosol substance in the lower atmosphere are in their annual average power significantly less than such relatively constant sources as soil dust, generation of particles by the sea surface and formation of particles directly in the atmosphere as a result of various chemical and especially photochemical processes.^{1,2} However, the explosive character of an eruption is important first of all for the region where it happens. The effect of the most powerful volcanic eruptions is especially important in the stratosphere, because it is observed there during a long time. Since 1980 there was at least three such eruptions: Sent-Helens (1980), El-Chichon (1982), and Pinatubo (1991). The satellite observations of the spreading of the eruptive cloud give a reliable data on its motion along the latitude of the eruption site and gradual spreading to higher latitudes with simultaneous sedimentation of aerosol matter from the altitude of 20–25 km to the tropopause. Eruptive gases can reach significantly higher altitudes,³ where they produce the smallest aerosol particles due to photochemical reactions. This process can influence on the aerosol composition of the stratosphere during more than two years, and the global filling of the stratosphere occurs during this process. But the behavior of the aerosol substance of volcanic origin at the altitudes less than 15 km is not reliably detected from satellite measurements. To do this, it is necessary to use airborne, balloonborne or ground-based observations. We have carried out balloonborne measurements after volcanic eruptions of Sent-Helens and El-Chichon.

The amount of volcanic aerosol matter in the troposphere is comparable and even less than that coming from other sources. However the chemical composition and the morphological structure of volcanic particles can essentially differ from other particles. This makes it possible to estimate their contribution to the total aerosol content in different regions and to observe their evolution. Most interesting, from this point of view, is the determination of the element composition of aerosol matter, since volcanos emit substance enriched by some chemical elements. Specific chemical composition of the volcanic aerosol influences the disperse composition of particles and their morphological structure. So aerosol measurements in the near-ground atmospheric layer near the fumarol sources, which emit a material close to the eruptive one in its composition, simulate the more large-scale processes of volcanic eruptions.

2. AEROSOL MEASUREMENTS IN THE NEAR-GROUND ATMOSPHERIC LAYER ON KAMCHATKA AND KURIL ISLANDS

Measurements were carried out by the Aerosol Physics Laboratory during summer and fall seasons since 1974 till 1982 in the regions of high volcanic activity, i.e., near the volcanos Klyuchevskoi, Gorelyi, Mutnovskii, and Karymskii as well as in the region of the Uzon-Geizer hydrothermal system.⁴ In 1982 measurements were also carried out on Kunashir island near the Tyatya volcano as well as in the near-water atmospheric layer along the ship route from Petropavlovsk-Kamchatskii to Kunashir.

Samplings were done with special filters following the technique described in Ref. 5. The volume of air pumping through a filter was 1 m³ and more for the majority of samples. The main portion of ultra clean filters we got from B.I. Ogorodnikov from L.Ya. Karpov Physical-Chemical Institute. The three-layer separating filters, filters of the FPAR type and the glass fiber filters were used for sampling and analyzing the organic component of aerosols.

Air bleeding was performed with a blower of PRV-type, "Shmel" vacuum cleaner and "Plyushch" membrane sampler. Then filters were handled using an electron microscope and were subject to spectral, absorption, neutron activation, and X-ray fluorescence analyses. The neutron activation analysis was carried out at the Institute of Nuclear Physics of Uzbekistan Academy of Sciences and at the Joint Institute for Nuclear Research in Dubna. To measure the disperse composition of aerosol the AZ-5 photoelectric counters were used. They are capable of operatively obtaining data on the number density and size distribution of particles with the diameter above 0.4 μm.

To process the samples with an electron microscope the exposed filters were dissolved in xylol, and then the films produced of the solution were transferred to a special net. Use of an electron microscope enabled the disperse and morphological analysis of aerosol structures. The size distribution function was reliably determined in the diameter range 0.01–1.0 μm. The number of particles of larger size observed was too small to judge the distribution function. The use of the optical microscope for processing the filters made transparent with xylol allowed us to expand the range of particles size detectable to tens of microns, however data on the disperse composition in the size range 0.5–0.8 μm are not enough reliable because of some specific properties of particles. The technique of the morphological analysis of aerosol samples is described in Ref. 6.

Spectral analysis of the aerosol substance that had been carried out using absorption spectra was primarily aimed at identification of such elements as Al, Fe, Mg, Mn, Ni, Co, Pb, Cr, and some others. The main bulk of data on the element composition of aerosol samples was obtained from neutron activation analysis. This method has the advantage that the organic components of the filter basis used for the collection of samples are not activated by thermal neutrons. The sensitivity threshold and the accuracy of the method were determined for the majority of elements by the presence of these elements in the matter of clean filters. Therefore the data were averaged, in some cases, over few samples and the results of the absorption analysis were used in order to provide better reliability of the results.

The concentration of some chemical compounds in samples was determined by means of IR spectral analysis of the solutions and films produced of the aerosol matter by washing it out with CCl_4 and bidistilled water. It was revealed that the content of organic components did not exceed in all samples studied the values $2\text{--}5\ \mu\text{g}/\text{m}^3$, therefore no more accurate determination of the classes of organic compounds was then carried out.

Low concentrations of anions SO_4^{2-} were also observed in the water soluble fraction of aerosol matter, mainly it was about $5\ \mu\text{g}/\text{m}^3$, and the concentration of cations NH_4^+ was less than $2\ \mu\text{g}/\text{m}^3$. Polarographic measurements of the concentration of SO_4^{2-} confirmed the assumption that the concentration of SO_4^{2-} rarely exceeded $10\ \mu\text{g}/\text{m}^3$. These data allow us to conclude that in the majority of fumarol eruptions the concentration of the ammonium sulfate and persulfate is quite low. It is obvious that significant portion of the anion SO_4^{2-} amount was not detected in the laboratory analysis because it was mainly contained in the sulfuric acid which evaporated from filters before the analysis.

The results of the analysis of aerosol samples from regions near fumarol emissions showed a great divergence between the contents of various chemical elements measured during different years and from different volcanos. However, some common features are observed in the contents of some elements in the aerosol matter. For example, in aerosol substance sampled during one and the same year relative content of the majority of elements is approximately the same, except for Ta, Au, and Sm. Closest are concentrations of Sb, Co, Zn, Rb, Ag, and Ca. The element composition of aerosols near geysers is essentially different than that in fumarol volcanic emissions. Thus, the concentrations of such elements as Fe, Ca, K, Br, Cu, Ce, Sb, Co, Cs, Yb, and Lu in aerosols near geysers are many times higher than in the aerosols of fumarol emissions. At the same time concentrations of Sr, Sc, Se, Zn, Ag, and La are close in aerosols of both origins. Concentrations of Fe, Sr, Th, Hf, Yb, Hg, Cs, Rb, and Ag from the volcanic dust aerosol collected in the plumes (North Break and Big Tolbachek Crack Eruption) are close to those in aerosols from the Geyser Valley. Elements K, Ca, Br, Cd, As, Mo, Sm, La, and Au were almost absent in aerosols from the volcanic dust zone, and Sc, Se, Sb, and Co significantly exceeded the concentrations of these elements in two other aerosol types. High correlation ($r > 0.50$) is observed between the contents of elements forming the low volatile compounds: Fe, Sc, Co, Th, Ce, Cs, Sr, and Hf in dust matter of volcanic eruptions and their relative content in the Earth's crust. This conclusion is in good agreement with the data from Ref. 7, except for Cs. The values of enrichment coefficients E_f for Br, Zn, Cu, Hg, As, and Sb forming volatile compounds are not as high as that for

elements observed in Ref. 7. Subdivision of the obtained data into two groups relative to Fe concentration values (low and high content of Fe) showed that E_f values (relative to Fe content) in the first group of data are close to those for almost all the elements studied in Ref. 7. To a certain degree this effect is caused by the fact that the main fraction of Fe is in larger particles, but the elements Br, Zn, Cu, Hg, As, and Sb are observed mainly in small ones. The aspiration coefficients for larger particles essentially depend on sampling technique and can be different in different studies. In Tables I–III one can see data on element composition of some samples that supplement the data from Refs. 2 and 4 and well illustrate the spatiotemporal inhomogeneity of the elements content in the near-ground layer.

TABLE Ia. List of the sample numbers for Table II.

No.	Site of the sample collection	Date and time of the sample collection
Kaldera Uzon:		
1	Eastern thermal field	23 / 7, 16.30
2	Place No. 3, oil plate	23 / 7, 18.00
3	Central place	5 / 8, 16.20
4	Central place	5 / 8, 19.00
5	Central place, alum plate	11 / 8, 14.00
6	Central place, Sapozhok source	11 / 8, 17.00
7	Main observation site	13 / 8, 18.00
8	Place No. 1, Sulfur lake	13 / 8, 16.00
9	The same	14 / 8
10	Nothern part of the ridge	2 / 8
11	The same	12 / 8
Geyser Valley:		
12	"Vkhod v ad" geyser	7–8 / 8
13	"Big" and "Small" geysers	8–9 / 8
14	"Pervenets" geyser	9 / 8
15	"Sakharnyi" and "Sosed" geysers	9 / 8
16	"Vitrazh nepostoyannyi" geyser	10 / 8
17	Mean concentrations of elements in samples collected in the Geyser Valley in 1974.	

TABLE Ib. List of the sample numbers for Table III.

No.	Site of the sample collection	Date and time of the sample collection
1	Gorelyi volcano	21 / 7, 14 h
2	Mutnovskii volcano	17 / 7, 9 h
2a	– " –	17 / 7, 9 h
3	– " –	14 h
4	– " –	21 / 7, 17 h
5	– " –	21 h
6	– " –	22 / 7, 5 h
7	– " –	9 h
8	– " –, near fumarol	29 / 7
9	– " –, sulfur tower	17 / 8
10	Klyuchevskoi volcano	17 / 8, 12 h
11	– " –, lava flow	14 h
12	– " –, Balinkina's break	19 / 8
13	Klyuchevskoi volcano	1974 r.
14	Bezymyannyi volcano	1974 r.
15	Tolbachek volcano	1976 r.

To reveal the element distribution in the particles of different size, the analysis of three-layer filters was carried out. The data on mass median size of particles containing some elements are given in Table IV, as an example. For the volcanic dust zone, the main portion of aerosol substance was in the layer entrapping particles with the diameter exceeding 1 μm practically for all the determined elements. The ratios of the element mass in large particles to their mass in small particles were the following, in fumarol samples: Se – 500, Lu – 100, Fe - 10, Mo - 13, Cr - 12, Au - 7, Cd - 5, Ta - 2, Ce - 2, Br - 1.6, K - 1, Yb - 0.5, Cs - 0.5, Sr < 0.3, Cu - 0.05, and Hg - 0.05.

Typical diurnal behavior that agreed with the diurnal behavior of the aerosol particles number density in the near ground atmospheric layer was observed for Cu in the Geyser Valley in summer with the daytime maximum near 3 p.m. and the nighttime minimum near midnight. Only one maximum of the concentration was observed for the elements Br, Cr, Ce, Cd, As, and Hg in the near-ground layer: for Cd, As, Hg, and Cs at 6–12 p.m., Br, Ta, and for Mo at 0 a.m., and Cr at 3 p.m., while the minimum of content of all these elements was observed in the near-ground atmospheric layer during nighttime from 0 till 7 a.m. No diurnal behavior of the concentration of other elements in the near ground layer was revealed. The observed diurnal behavior of the element

concentration can be explained by the condensation and coagulation growth of particles containing these elements during evening and night. One can suppose that the aforementioned elements are washed out more easy than the others.

Essential differences are revealed in the chemical composition of aerosols of volcanic origin in different geographical regions. As is seen from Table V, the variations can reach 2 to 4 orders of magnitude for some elements. One can say at certain that aerosol of Tolbachek eruption (1976) were evidently rich of Hf, Sc, La, Cr, and Zn, but at the same time contents of Cs, Cu, As, Sb, and Hg were higher and comparable with those in the aerosols from Ethna and Augustin eruptions happened in the same year. This, evidently, allowed one to suppose that either the sources of emitted matter were close in their depths and composition or that there existed a mechanism of the planetary significance which worked in different regions of the Earth producing the eruptions in 1976. It is worth noting that the aerosol in the Ethna region was enriched with S while there was no sulfur observed in the aerosol from Tolbachek eruption at all. At the same time, high content of Cu in aerosols from Tolbachek eruption (1976) well agreed with specific feature of high Cu content in the high temperature sublimations which abundantly fell out in the North Break crater of this eruption, as was noted by volcanologists.⁸

TABLE II. Concentration of elements in the air samples (ng/m³) taken in the Geyzer Valley.

No.	Chemical elements																
	Ag	Au	Ba	Br	Cd	Co	Cr	Cs	Fe	Hg	La	Na	Ni	Rb	Sb	Sc	Zn
2	—	1.6	—	2400	—	80	50	—	—	1200	—	—	—	—	183	2.7	+
5	180	4.6	—	5900	—	98	60	—	49r	8500	—	—	—	—	63	2.6	+
6	—	1.8	—	—	—	114	60	—	73r	2200	143	—	—	—	96	1.7	+
10	—	—	—	—	—	—	—	—	27T	—	—	—	—	—	118	0.4	4100
11	—	—	—	—	—	—	—	—	—	—	—	—	—	—	43	—	—
8	—	0.7	—	—	—	—	—	20	18	—	—	—	—	800	600	—	—
9	—	106	+	—	—	—	—	+	—	—	+	—	—	+	80	—	2300
7	—	0.4	—	—	—	—	—	—	—	—	—	—	—	—	83	0.5	—
1	—	2	—	600	—	440	220	63	200r	21r	2	—	—	—	79	0.5	1600
3	—	0.4	—	—	—	—	10	—	—	—	—	—	—	—	—	—	100
4	—	0.4	—	870	—	8	20	—	—	—	—	—	—	—	8	0.7	—
12	—	—	—	—	—	67	—	—	—	—	+	+	—	—	7	1.0	—
13	+	—	+	—	+	1	—	—	30r	—	—	+	+	—	1120	—	970
14	—	—	—	—	—	—	—	+	—	—	+	+	+	+	84	0.1	900
15	—	—	—	—	—	—	—	—	—	—	+	+	—	—	—	0.7	—
16	+	0.2	+	—	—	—	—	—	+	—	+	+	+	+	9	—	350
17	50	22	—	5500	1400	120	—	41	180r	210	10	25r	—	70	120	23	—

Note: Symbol "+" denotes that element was detected, but quantity was not determined, "—" — that element was not detected, and "r" denotes 1000 μg/m³.

TABLE III. Concentration of elements in the air samples (μg/m³) taken in the region of volcanos in 1980.

No.	Chemical elements																	
	Ag	Au	Br	Cd	Co	Cr	Cs	Fe	Hf	Hg	La	Na	Ni	Rb	Sb	Sc	Sm	Zn
1	—	—	120	—	162	20	—	53000	—	480	20	—	—	—	35	4.2	—	5500
2	—	4.9	3130	—	—	390	10	17000	—	—	—	—	—	—	—	1.9	—	—
2a	—	6.8	3440	—	—	590	—	9000	—	—	—	—	—	—	—	1.6	—	—
3	—	2.4	—	—	—	5100	—	—	—	—	—	—	—	—	287	—	—	—
4	—	—	117	710	104	—	—	23000	—	150	10	—	—	—	31	2.1	—	+
5	149	2.6	11	28	—	110	—	6300	—	100	2	650	—	—	21	0.2	0.9	20
6	4	0.4	226	—	30	77	—	79000	—	—	5	—	—	63	7	0.4	—	200
7	—	1.7	—	—	—	—	—	—	—	—	—	—	—	—	3970	—	—	—
8	46	1.0	—	47	—	120	—	1800	—	—	2	—	100	—	5	0.3	3	—
9	362	3.4	—	—	—	450	—	—	—	530	+	—	620	—	79	—	—	—
10	—	4.0	7600	—	760	50	—	59000	—	1500	—	—	—	—	58	7.3	—	4750
11	—	2.8	6800	—	680	110	—	—	34	—	—	—	—	—	58	4.1	—	+
12	—	—	—	—	—	—	—	—	—	—	—	—	—	—	9500	—	—	—

TABLE III. (continued)

Average concentrations of elements in the samples taken near fumarol exits in 1974–1976																		
13	50	6.3	680	220	25	—	10	30000	8	54	8.5	3200	—	100	50	23	380	300
14	50	60	2400	900	26	—	15	50000	11	240	8.5	15000	—	100	50	17	230	300
15	52	—	500	500	560	—	68	12000	32	250	—	12000	—	62	320	140	100	130
								0										

Samples taken near geysers revealed similar size-distributions of aerosol particles. The first maximum of the size-distribution function is in the range 0.03–0.05 μm , the second one is in the range 0.15–0.20 μm , and the third one in the range 1.5–3.0 μm . Such a shape of the size-distribution function is in a good agreement with the classical concept about a three-mode distribution of aerosol particles in the atmosphere. It is also characteristic of fumarol eruptions.

TABLE IV. Values of the mass median aerodynamic diameters (MMAD) and their standard geometric deviations in aerosols from the Mutnovskii volcano.

Element	MMAD, μm	σ
Cr	0.5, 0.7	1.9, 3.6
Fe	0.4	9.9
Sc	0.5	—
Co	0.5	1.2
Sb	0.8	1.2
Au	0.8	1.0
Th	1.0	1.1

We did not observe the three-mode particle size-distribution functions in the dust volcanic eruptions. The shape of the size-distribution functions changes noticeably depending on the eruption intensity and on the time and site of the sampling. The first and the second modes are inseparable, but the third mode is quite well pronounced. The maximum of distribution can shift towards larger size [up to 10 μm and more (Fig. 1)].

The results of the comparative analysis of the morphological structure of aerosols of volcanic and fumarol origin is of special interest. One should note a relatively high content of aggregates—fractals and particles of coagulative origin (discontinuous spheres, loose particles with irregular shape and chains). The coagulants consisting of large particles are also characteristic of volcanic aerosols.

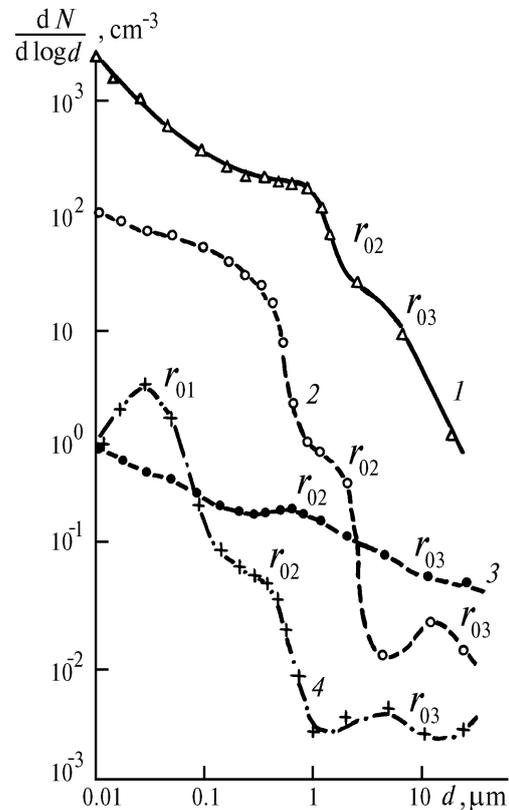


FIG. 1. Typical particle size-distributions for the aerosol of volcanic origin: 1) dust cloud near eruption, $l = 3$ km (July 1976, North Break), 2) dust cloud far from eruption, $l \sim 15$ km (July 1976, North Break), 3) Gorelyi volcano eruption (July 1980), and 4) Fumarol emission (August 1974, Steller's crater, Klyuchevskoi volcano).

TABLE V. Enrichment coefficients E_f of different elements in aerosol matter in volcanic eruptions relative to their content in soil. (It is supposed according to Ref. 4 that $E_f = 1$ for Al, Si, and Fe.)

Chemical element	Volcanos								
	Izalko (1966)	Himaeu	Kilaue	Meion	Arenal	Ethna	Tolbachek (1976) Ref. 4	Tolbachek (1976) Ref. 7	Augustin (1976)
K	0.056	—	—	—	0.03	8.9	0.15	—	0.43
Na	0.190	—	—	0.04	0.08	15.0	2	1.9	1.30
Mg	0.300	—	—	0.27	0.13	—	—	—	0.78
Mn	0.026	—	—	—	—	5.9	—	—	0.78
Sc	—	0.90	—	—	—	0.3	5	1.6	1.50
La	—	0.40	—	—	—	—	—	4.1	0.69
V	—	—	—	—	—	2.4	—	—	1.60
Co	—	3.30	—	—	—	4.4	8	4.0	0.75
Hf	—	0.40	—	—	—	—	7.5	16.8	—
Cr	—	—	—	—	—	2.8	—	32.0	7.50
J	—	—	—	—	—	—	—	30.8	—
Cs	—	—	—	—	—	20	175	1620	—
Zn	—	53	—	—	—	580	0.8	950	4.30
Pb	—	—	—	—	—	320	—	—	20
Cu	—	—	—	—	—	240	120	2200	13
Cd	—	—	—	—	—	1900	1250	—	233
S	—	—	—	60	13	11	—	—	—
As	—	—	—	—	—	800	250	2780	173
Sb	—	115	17000	—	—	660	8000	11	84
Se	—	—	—	—	—	180000	1950	—	—
Cl	—	—	—	—	25	31000	—	28.5	17–8000
Br	—	—	—	—	—	36000	125	230	1060
Hg	—	—	35000	—	—	13000	50000	2740	50000

Note: Symbol "—" means that the element was not detected.

3. BALLOONBORNE IMPACTOR MEASUREMENTS

The technique and results of balloonborne impactor measurements are described in Refs. 9–11. Collection of aerosol particles was made by means of impactors equipped with the continuously moving base with the formware coating, under which the grids for electron microscopy were placed. The motion of the base under the chink nozzle oriented by the wide face perpendicularly to the base motion direction makes it possible to obtain the temporal or (if one have the data on the height of the rise of a rocket or a balloon) spatial behavior of the aerosol sampling. The two-cascade impactor with a forced air pumping by the MRG–4M inducer was used in the balloonborne measurements. The nozzle width was 0.3 mm in the first cascade and 0.1 mm in the second one. The efficiency of particles settling in both cascades was estimated by the value of the inertial parameter:

$$\psi = \frac{2C \rho_p v_p r_p^2}{9 \eta D}$$

where r_p is the particle radius, C is the Cunningham correction coefficient depending on the density ρ_p and size of particles, η is viscosity, D is the nozzle width at the output, v_p is the linear speed of a particle near the nozzle output. The calculations show that particles with $d \approx 0.1 \mu\text{m}$ can settle on the base of the second cascade. One can suppose that the efficiency of particles settling is equal to 1 for the particles with $d > 0.10 \mu\text{m}$, taking into account the measurement error.

The disperse and morphological analysis of stratospheric aerosols was carried with a transmission electron microscope–microanalyzer EMNA–2. The disperse

analysis was carried out for the particles with d from 0.002 to 2 μm at three magnifications (50000, 20000, and 10000 times). Particles smaller than 0.002 μm were not analyzed since such particles are low contrasting due to the finite thickness of the formware film. The particle size was determined as the mean value of the diameters of a particle cross section in different directions. The particle size distributions for separate flights were unstable and multi-mode due to small amount of particles collected at a height level as well as because of a strong variability of their disperse composition in a limited air volume. Averaging of the distributions over the layers of 5 km allows us to reveal some features in the altitude behavior of the particle size distribution (Fig. 2).

In addition to the fact that the particles number density in the stratosphere just after a volcanic eruption is significantly greater than the annual average background values of the number density of particles of different size, and their spectrum is essentially transformed since it is formed mainly by the condensation processes in the presence of particles of the disperse origin, while the coagulation mechanism of the spectrum formation does not yet work. An evident increase of the fraction of large particles is revealed in the averaged data what is indicative of the increase of contribution coming from particles of the eruptive origin. However, the mode at $d = 0.15 \mu\text{m}$ is practically absent at the heights above 35 km. One can suppose that it appears either due to heterogeneous reactions in the atmosphere on the surface of nuclei already present in it or due to coagulation of smaller particles. The absence of maximum in the distribution in the range $d = 0.02 \mu\text{m}$ is indicative of the aerosol generation from the gas phase: condensation of the sulfuric acid vapor for the lower stratosphere and condensation of the evaporated substance in the higher layers.

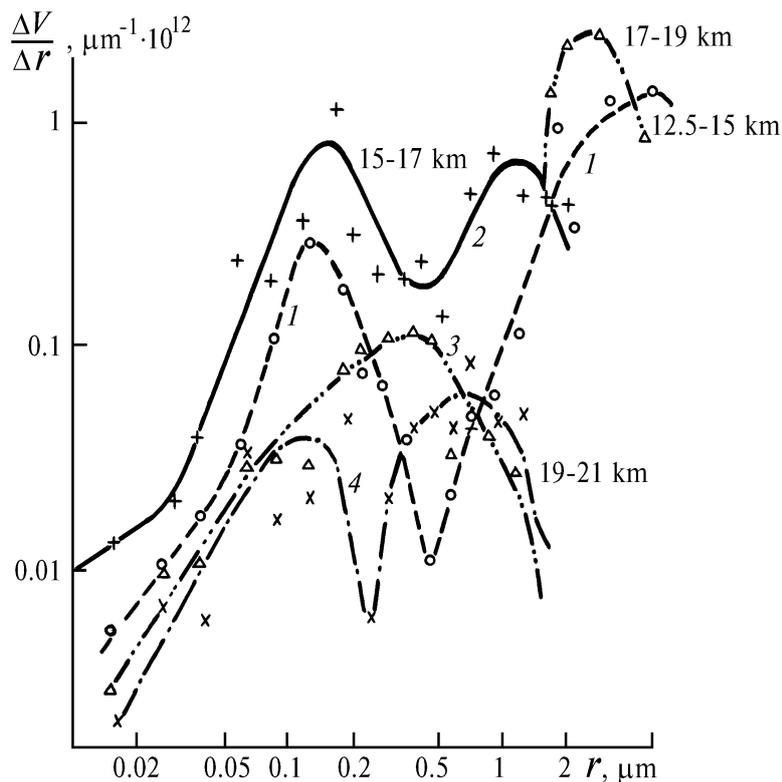


FIG. 2. Volume particle size-distribution functions dV/dr for stratospheric aerosols observed after Mt. El-Chichon eruption in the stratosphere (balloonborne measurements 1982-85, Ryl'sk): 1) 12.5-15 km is shown by \circ , 2) 15-17 km is shown by $+$, 3) 17-19 km is shown by Δ , 4) 19-21 km is shown by \times .

The data on the spectra obtained are in good agreement with theoretical ones for conditions when there is a constant vapor source in the atmosphere that can cause supersaturation and homogeneous formation of droplets. At some moment the rate of consumption of vapor by droplets can become comparable with its production rate and even exceed it. As a result, formation of droplets stops and the size spectrum shifts, during some time, towards larger size as a whole.

The morphological electron microscopic analysis of aerosol samples shows that the particles microstructure changes with the increase of height follow certain regularities. Thus, particles of soil origin with irregular shapes are characteristic of the lower layers, microcrystals of various shapes can also be found there, spherical droplets of sulfates "rosettes" and dense coagulants covered with liquid water shields occur in the troposphere. A large fraction of the low stratospheric aerosol are small homogeneous particles of spherical shape and "chains". At altitudes above 25 km the fraction of chains sharply increases. Homogeneous spheres with $d = 0.03 \mu\text{m}$, which are relatively

low contrasting, presumably of sulfuric acid, and the spheres with $d \sim 0.01 \mu\text{m}$ with high specific density, evidently, of the ferric oxides are also observed here. The fraction of nonspherical particles, mainly "chains" is of the order of 5-10% at the height of 20 km, and 15-25% at 30 km and higher. It is quite probable that a portion of "chains" is destroyed when settling on the base. Therefore, in fact their portion can be significantly higher. The portion of crystals is not large and does not exceed 5% at the height of 5 km for the majority of flights.

The morphological electron microscopic analysis of samples shows essential changes of the stratospheric aerosol microstructure during the period under consideration. High fraction of particles with chain structure is typically observed in measurements during the period before a powerful volcanic eruption. They consist of spheres with relatively homogeneous density and size containing ferric oxides and of the complex chain structures which are characteristic of the smokes consisting of the less dense matter (possibly, soot). The fraction of large spheres, which are packed conglomerates of

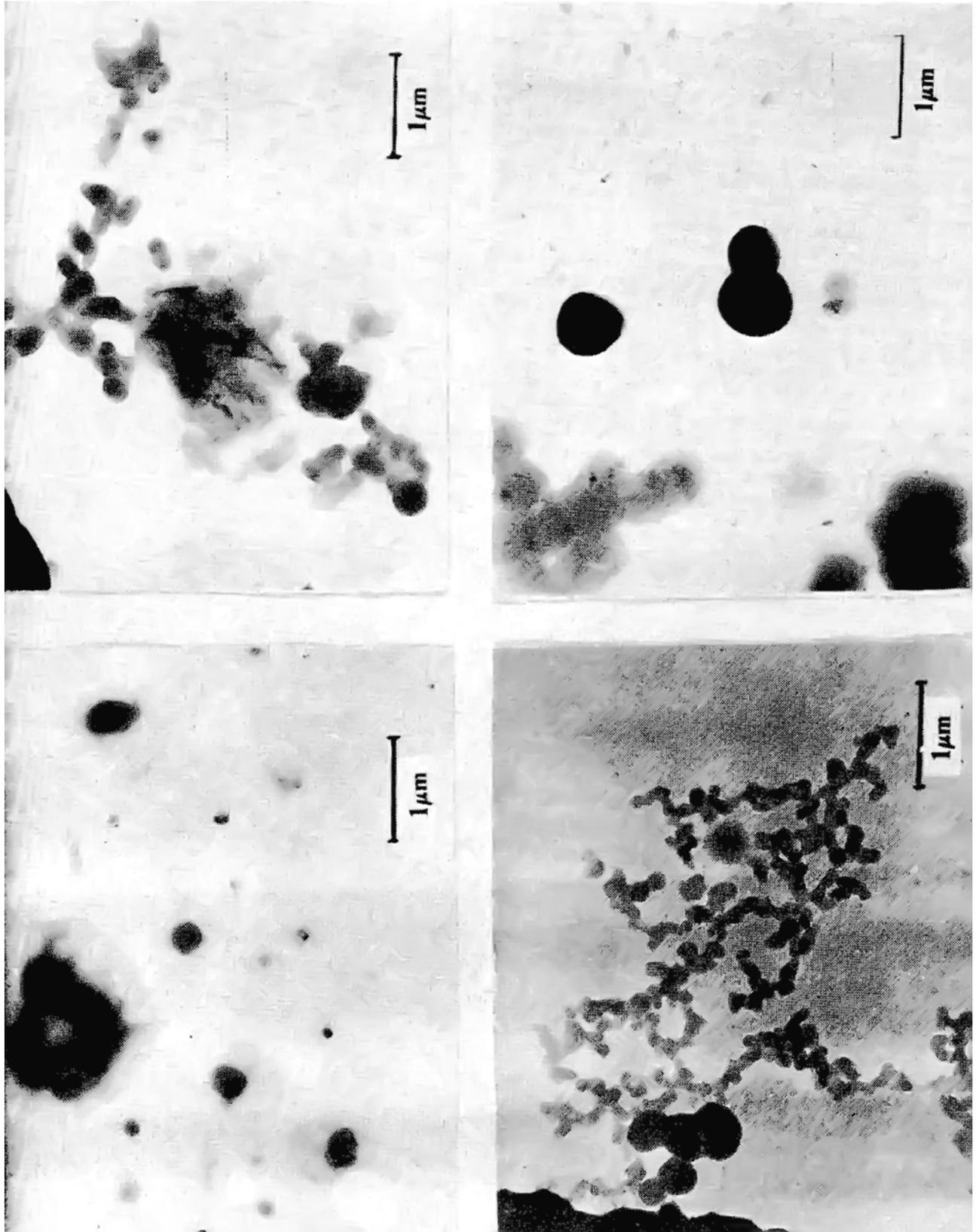


FIG. 3a. Electron microscopic pictures of different types of aerosol particles (1984) at the heights below 14 km.

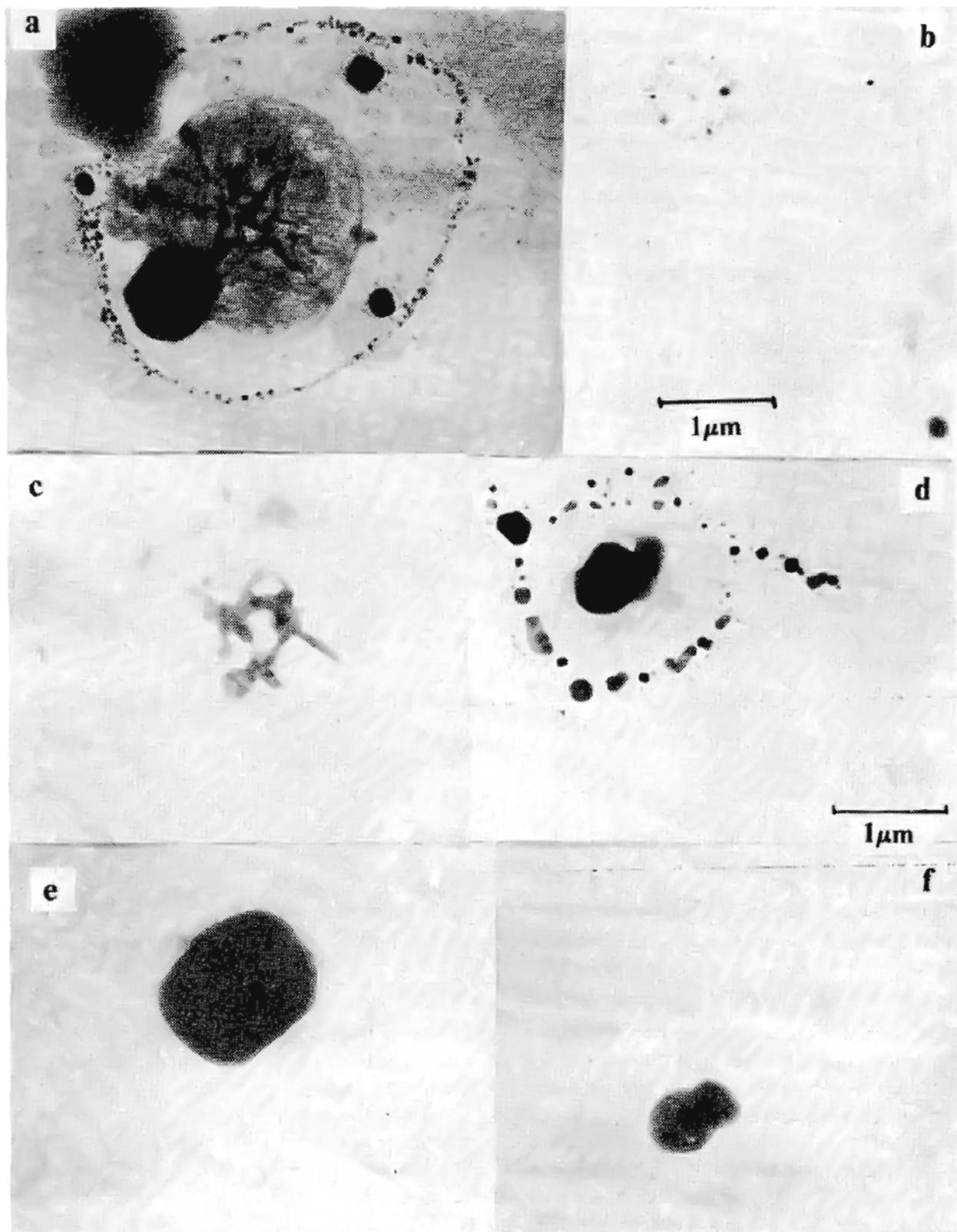


FIG. 3b. Electron microscopic pictures of different types of aerosol particles (1984) at the heights above 14 km.

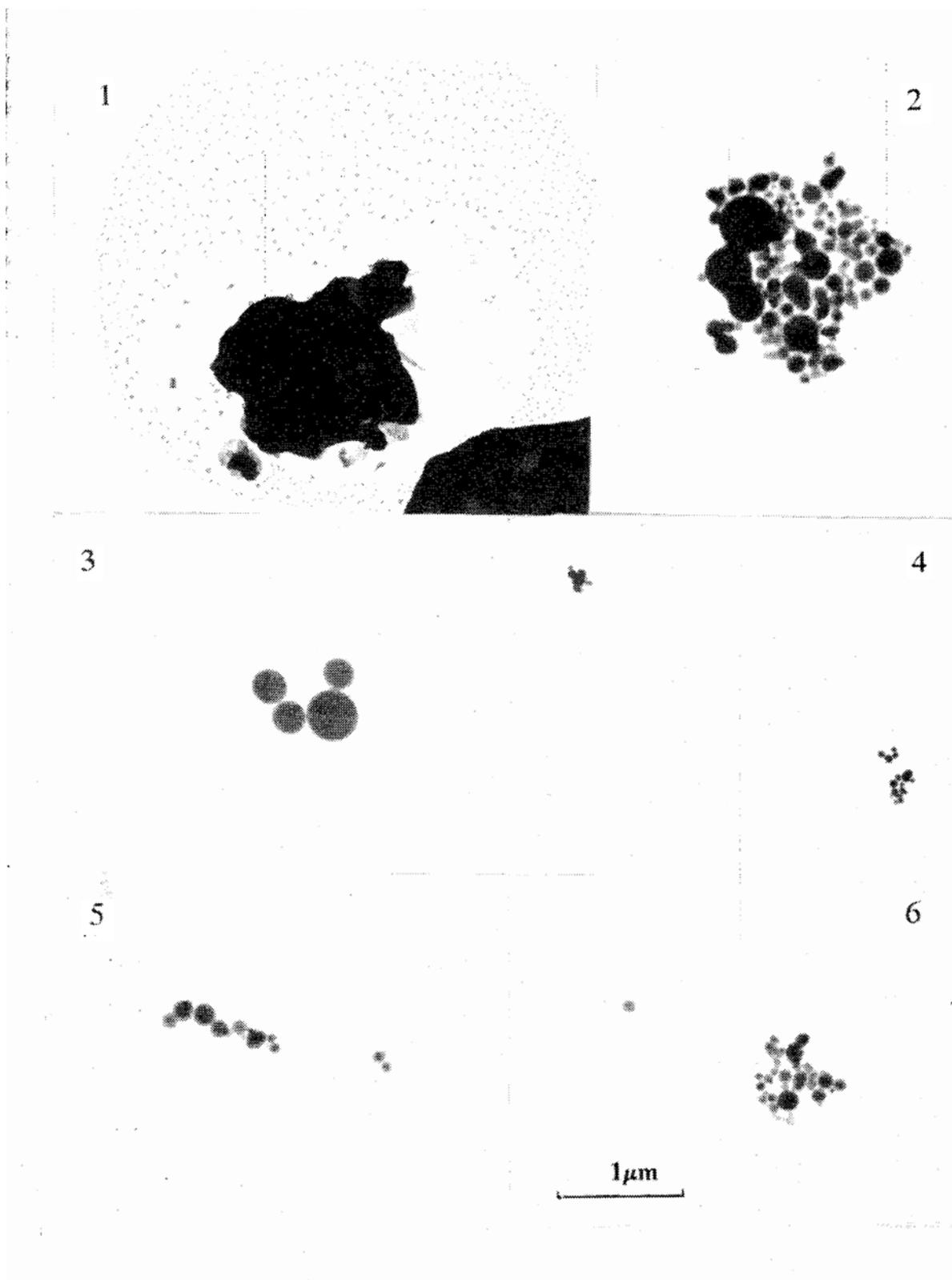


FIG. 3c. Electron microscopic pictures of different types of aerosol particles (1984) at the heights above 23 km.

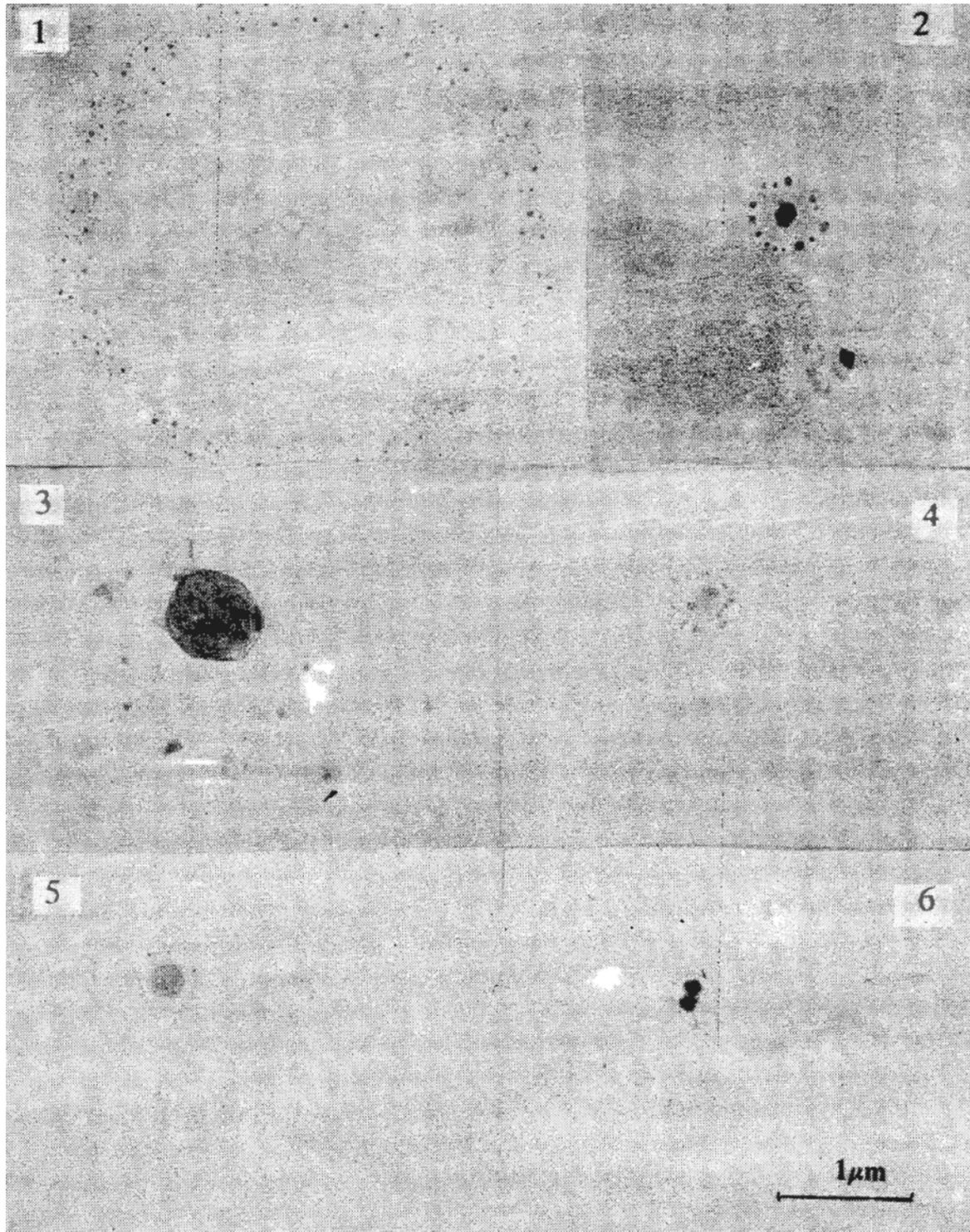


FIG. 3d. Sulfuric acid droplets with microcrystals around their surface observed at the height of 20 km.

particles of different chemical composition (including sulfates), is relatively large.

The fraction of "chains" decreases, while that of loose spheres increases during the period after an eruption. Significant amount of sulfuric acid droplets (Fig. 3) is revealed in the aerosol layer at heights above 20 km. The classical structures of the sulfuric acid particles of relatively large size, composed of nucleus and a shield of many small

particles, mostly crystals, were observed in measurements of 1984–1985, more than two years after the El-Chichon eruption. The height where the maximum content of sulfuric acid particles was observed fell down to 20 km. The heterogeneous formations of crystal nuclei covered with the solution of sulfuric acid were also observed here. These are more stable and old structures. The fraction of chain formations is also high. Highly dense and homogeneous

spheres were mainly observed at the heights above 30 km. The spheres often had almost equal preferred size.

The results of morphological analysis of balloonborne samples collected during the Soviet–American experiment in Ryl'sk, 1987 turned to be very unusual. The sharp decrease of the fraction of sulfuric acid and sulfate particles in the lower stratosphere was revealed. The most characteristic structures were either separate dense spheres or chains of smaller dense spheres. This makes us to suppose that the generation of aerosol particles from the gas phase was not observed in the stratosphere in 1987, but the accumulation of solid particles of different origin occurred.

The measurements conducted in spring, 1989 (Apatity) showed practical absence, in the stratosphere, of the aerosol particles which could be identified as being produced due to the emission of solid volcanic particles. The sulfuric acid and sulfate particles, primarily the ammonium sulfate particles of low density made up the main portion of particles.

The particles close in the morphological structure were observed in measurements of 1982 at the height about 30 km

where, obviously, the homogeneous formation of the sulfuric acid droplets occurred. Their significant decrease occurred only in the fall, 1984. Analysis of the chemical composition of stratospheric aerosols in samples taken before 1982 by using an IR spectroscopy technique showed that the mass concentration of aerosols was insufficient for determining any components at certain.

The absorption bands at the wavelengths near $9\ \mu\text{m}$, which are characteristic of the SO_4^{2-} group, were distinctly observed in the IR spectra of samples collected in the fall of 1982. These bands were more pronounced in samples taken at the heights above 20 km than in samples taken at 5 km height. Approximate estimates of the sulfuric acid concentration at the height of 22–23 km gave the value exceeding $2\ \mu\text{g}/\text{m}^3$. The element analysis of the samples was carried out by different nuclear physics methods: neutron activation, proton activation, and X-ray fluorescence. The data on the content of some elements in the atmosphere for the balloonborne impactor samples of 1983 and 1984 are shown in Fig. 4.

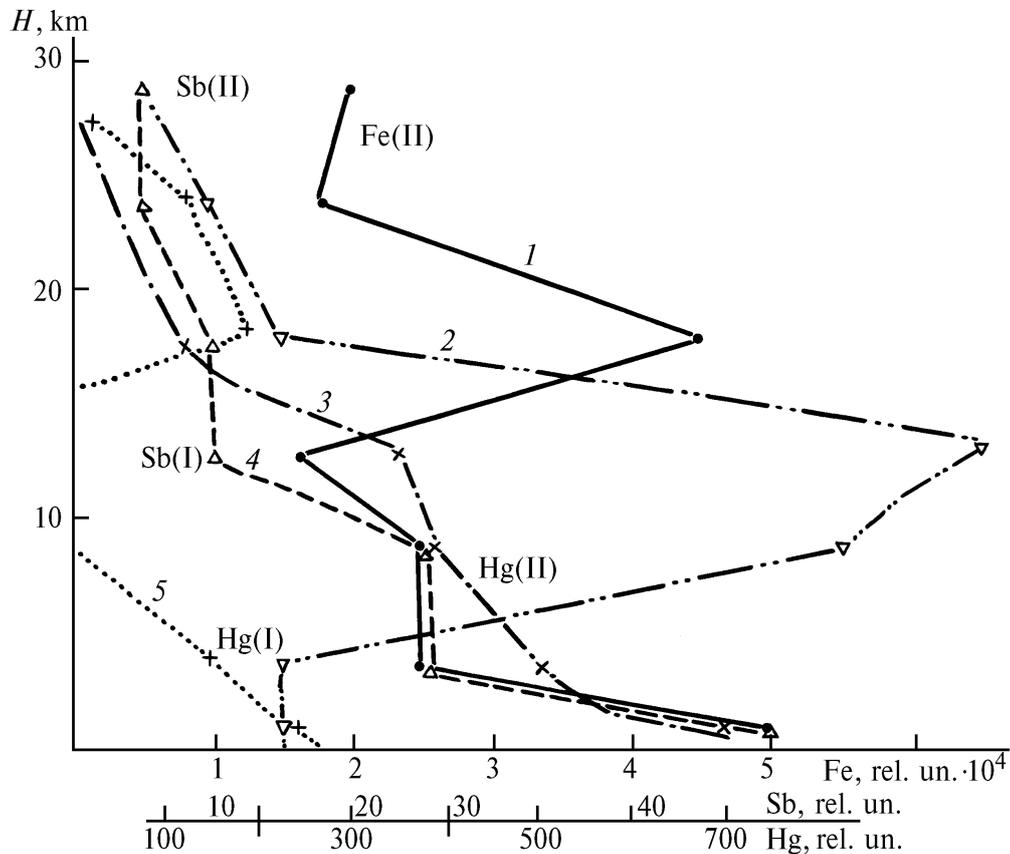


FIG. 4 Vertical profiles of the content of some elements in the atmospheric aerosols (1983–84): first cascade (I); second cascade (II); 1) Fe, 2) Sb (II), 3) Hg (II), 4) Sb (I), and 5) Hg (I).

The Junge aerosol layer is distinctly seen in the profiles of all the elements studied. Some evolution of the content of these elements is observed starting from 1983 and 1984. One should pay especial attention to a very high content of Sb in the stratosphere after El–Chichon eruption. The enrichment of volcanic emissions by this element is of the order of 10^4 – 10^6 . At the same time, in measurements of 1983 we observed lower content of Fe than in measurements of 1984. One can suppose that in 1983 Fe was intensively washed out from the stratosphere

because of quick growth of the particles containing it due to catalytic reactions of oxidation of SO_2 to SO_3 . Analogous behavior is observed for Sc. Quite high content of elements, which are not characteristic of the sulfate and sulfuric acid particles, being at the same time, good catalysts of the reactions of oxidation of sulfuric compositions, makes us to suppose that the homogeneous mechanism of aerosol formation from sulfuric acid can hardly be dominating among the processes of the stratospheric aerosol formation.

TABLE VI. Enrichment coefficients of different elements in aerosol matter of volcanic eruptions, normalized to Fe.

Element	Volcano		
	Augustin 6 km	El-Chichon 10 km	1983–1984 25 km
Sb	84	3000	2700
Se	—	1200	14000
Cd	233	16000	10000
Ag	—	6000	20000
Hg	5000	26000	240
Br	1060	25	4
Cr	7.5	7.5	1.7
Zn	4.3	14	2
Cs	—	3	0.4
Co	0.75	2.5	0.23
La	—	0.5	0.12
Sm	—	2.8	0.12
Sc	1.6	0.01	0.00033

One should note principle difference in vertical distributions of heavy metals, Hg, Sc, Fe, and Cd, and such volatile elements characteristic of the volcanic eruptions as Sb and Se. The maxima of distributions of the latter ones are at higher altitudes. The lowest is the layer of maximum concentration of Hg, it is at the height of 13–14 km for 1983 and 1984. Most distinctly the differences in element composition of aerosols are seen from the data on the enrichment factor (relative to Fe). Data on the enrichment factor for altitudes of 10 and 25 km as well as on the element concentrations averaged over measurement series of 1983 and 1984 are given in Table VI along with the data on the enrichment factor for other volcanos. Very good agreement is observed in the values of enrichment factor for the height of 10 km and E_f for the Augustin volcano while significant difference between them is observed for the height of 25 km. Very good agreement is observed for Cr, Zn, and Co. A significant decrease of E_f is characteristic of Br and Sc, especially Sc, i.e., sharp decrease of the concentration of these elements with height occurs.

4. CONCLUSION

Analysis of the results of direct measurements of aerosols in different atmospheric layers before and after volcanic eruptions allows us to correct the assumption on the possibility of separating of the contribution of volcanic eruptions into the aerosol component of the atmosphere. The

problem is in fact much more complicated and has no single solution.

1. The disperse composition of particles of volcanic origin has no any distinct peculiarities, at least for the lower layers of the atmosphere. It is characteristic of the stratosphere that the mode of large particles ($d > 0.3 \mu\text{m}$) of the eruptive origin appear in the aerosol size distribution at the early stage of the volcanic cloud formation, as well as the presence of a large amount of small ($d < 0.02 \mu\text{m}$) particles of the condensation origin. Their modal radius gradually shifts towards larger values.

2. The morphological structure of volcanic aerosol undoubtedly has a number of specific features which also change during the particles life. At the initial stage it is the presence of a large amount of sulfuric acid droplets, aggregates of small particles typical for smokes, and the particles of irregular shapes. At the later stage it is the appearance of double layer particle structures with the outer layer of microcrystals.

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